



Hydrogen generation by the hydrolysis reaction of ball-milled aluminium–lithium alloys



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HIGHLIGHTS

- The hydrogen generation rate of Al–Li alloys (Li < 10%) is enhanced significantly.
- The hydrogen yields of Al–Li alloys (Li < 10%) can reach 100%.
- Al–Li alloys (Li < 10%) can react with water at different temperature to produce H₂.
- The cost of hydrogen generation for Al–Li alloys is reduced.

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ABSTRACT

The addition of Li can prevent an inert alumina film from forming on the surface of Al alloy particles, allowing the rapid hydrogen generation of Al alloys to be achieved. However, because the Li content is less than 10%, the hydrogen generation rate and hydrogen yield of Al–Li alloys are significantly decreased. In this work, NaCl is introduced to prepare Al–Li alloys with low Li contents by ball milling. The research results show that by increasing the amount of NaCl added, the ball milling time and Li content can effectively improve the hydrogen generation of the alloys. Under optimal preparation conditions, the ultimate hydrogen yield of Al–Li alloys can reach 100%. The initial water temperature has almost no effect on the generation of hydrogen, even at 0 °C. Ca²⁺ and Mg²⁺ can combine with OH[−] to form the insoluble compounds Ca(OH)₂ and Mg(OH)₂, which can prevent hydrogen generation. NO₃[−] reacts with Al to form ammonia and reduce the hydrogen yield of the alloys. Therefore, Al–Li alloys should be prevented from reacting with water containing Ca²⁺, Mg²⁺ and NO₃[−]. Al–Li alloys must be stored in isolation from air to maintain good hydrogen-generation performances.

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1. Introduction

Automobiles offer a fast and convenient mode of travel to suit modern lifestyles. However, at the same time, individuals are concerned about the exhaust that automobiles produce. To reduce the emissions of greenhouse and polluting gases, it is urgent that we find a renewable and clean fuel to meet energy demand. Hydrogen possesses a high mass energy density that is three times that of gasoline. More importantly, when used as a fuel, hydrogen does not emit any pollution gas. Therefore, hydrogen may be a promising alternative fuel for automobiles in the future [1].

However, hydrogen must first be prepared by a traditional method and then delivered to the user in the form of a liquid or compressed gas. Some potential hazards arise in the process of storing and delivering hydrogen due to its flammable and explosive properties. Therefore, the rapid production, safe storage and delivery of hydrogen have become the main problems hindering the development of hydrogen-based automobiles [2]. If liquid or compressed hydrogen can be replaced by hydrogen-producing materials to provide hydrogen for automobiles, the safety of mobile hydrogen systems will be significantly improved.

Some metals and their alloys, such as Mg-based, Al-based, Zn-based and Fe-based materials, exhibit good activity and can react with water rapidly to produce hydrogen [3–6]. Among these materials, aluminium is inexpensive due to its abundance in the earth and has a low atomic weight (27 g mol^{−1}), 3 valence electrons and high activity [7]. As 1 mol or 27 g of aluminium reacts with water, it

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can produce 1.5 mol of hydrogen. The hydrogen density of aluminium (the hydrogen production of unit mass materials) can reach 11.1% and is only below that of Li (14.5 wt.%), among all other metals. Additionally, the products of the reaction between Al and water, Al_2O_3 or $\text{Al}(\text{OH})_3$ are easily recycled by mature metallurgical processes [8]. Therefore, aluminium is the most promising material for future hydrogen generation.

Although aluminium exhibits a strong thermodynamic reaction with water when producing hydrogen, an inert oxide film easily forms on the Al surface, preventing further water from contacting the Al metal surface in near-neutral-pH water solutions and hindering the continued production of hydrogen [9]. This self-protection property, i.e., the formation of an inert oxide film, offers an advantage against continued corrosion when aluminium is used as a structural material [10]. However, this property significantly affects hydrogen generation by the hydrolysis reaction of aluminium. Therefore, the development of a method for destroying the inert oxide film or preventing it from forming on the Al surface has become the key to achieving the rapid generation of hydrogen.

Many methods have been adopted by researchers to destroy this inert oxide film. For example, either a NaOH or NaAlO₂ solution can be used to dissolve the alumina film [11,12]. Although hydrogen can be produced rapidly, such a method is difficult to apply in mobile hydrogen systems due to the highly corrosive nature of the reaction solution. As a result, some researchers have begun to study the activation and modification of aluminium. Either NaCl or Al_2O_3 is used to activate aluminium by ball milling [13,14]. However, only as the amount of added NaCl or Al_2O_3 addition reaches 76 wt.% or 90 wt.%, respectively, can a hydrogen yield of 100% or 70% be obtained with Al-based materials. Furthermore, these additions cannot produce hydrogen by themselves, thus significantly reducing the hydrogen produced per unit mass. Hence, the materials are also unsuitable for use in mobile hydrogen production. Research results have shown that the preparation of Al alloys, such as Al–Sn alloy, Al–In alloy and Al–Bi alloy, can alter the existing form of Al and prevent the formation of an inert oxide film [15–17]. In particular, Woodall, a professor at Yale University, observed that Al easily dissolves in Ga metal, forming Al–Ga alloy. Al is dispersed in the alloy at an atomic level, preventing the inert alumina film from forming [18]. As a result, Al–Ga alloy can react with water to produce hydrogen rapidly. However, only when the Ga content is sufficiently high (72 wt.%) can the hydrogen yield of Al reach 100%. Because Ga metal is not only very expensive but also cannot produce hydrogen by itself, the hydrogen density per unit mass of Al–Ga alloy is very low, and the cost of hydrogen generation is high. Ilyukhina et al. [19] and Parmuzina and Kravchenko [20] added low-melting-point metals such as In and Sn to improve the activity and decrease the Ga content of an alloy prepared by the ball-milling method. The research results showed that the Ga content of the alloy was significantly reduced to 10 wt.% and that the prepared Al–10 wt.%Ga–4.3 wt.%In and Al–10 wt.%Ga–4.2 wt.%In–1.7 wt.%Sn–0.8 wt.%Zn powder could react with water to generate hydrogen with 90% hydrogen yield. However, the addition of expensive rare metals not only increases the cost of hydrogen generation but also makes the byproducts complex, causing them to be more difficult to recycle. Therefore, it is necessary to develop new Al-based materials for hydrogen generation.

Li is an active metal that can react with water to produce hydrogen by itself and has a very high hydrogen density (14.5%). Therefore, Li can be added to preparations of Al–Li alloy to improve the activity of Al. In our previous research [21], an Al–Li alloy was prepared using a melting method. Because the Li contents ranged from 10 wt.% to 20 wt.%, the hydrogen yield of the alloy was almost able to reach 100%. In addition, Fan [22] prepared an Al–Li alloy by ball milling. Only as the Li content of the alloy reached 30 wt.% could the hydrogen yield of the alloy reach 92%. If the Li content is

decreased to 20 wt.%, the hydrogen yield of the alloy will be significantly reduced. To improve the hydrogen yield of Al–Li alloy with a low Li content (<20 wt.%), rare metals such as Bi, Sn and In or compounds such as NaBH_4 and CoCl_2 are incorporated into the alloy by ball milling [23]. Although the hydrogen yield is improved, the composition of the alloy becomes more complex, which causes some difficulties when recycling the metal. Generally, Li can improve the activity of Al. However, the Li content of the aforementioned Al–Li alloy is still high, which causes the cost of hydrogen generation to increase due to the high cost of Li. Only by decreasing the Li content of the alloy can the cost of hydrogen generation be effectively reduced.

However, as indicated by our work and that of Fan, the effect of the Li content on the hydrogen yield of the alloy is significant, and the hydrogen generation rate and hydrogen yield of Al–Li alloys can be reduced with decreasing Li content. To achieve the rapid generation of hydrogen using an Al–Li alloy with a low Li content, the alloy preparation method is critical. In this study, an Al–Li alloy with a low Li content was prepared by the ball-milling method. The effects of the preparation conditions and reaction conditions on the hydrogen generation of the resulting Al–Li alloy were investigated.

2. Experimental

Al–20 wt.%Li (99.5 wt.%, 250 μm), Al (99.9 wt.%, analytical grade, 150 μm) and NaCl (99.8 wt.%, analytical grade, 140 μm) are used as the starting materials for the preparation of an Al–Li alloy by the ball-milling method. Ball milling was performed in a planetary ball miller (Qm-1SP-2, Nanjing University Instrument Plant, China) equipped with 500-ml stainless steel milling jars and steel balls measuring 4–5 mm in diameter. In each experiment, 20-g mixtures of Al–20 wt.%Li, Al and NaCl combined in different ratios and approximately 200 g steel balls were charged into the jars. During the process of ball milling, the rotational milling speed was maintained at 40 Hz, and the milling time was varied from 0.5 h to 4.0 h. Scanning electron microscopy (SEM, JSM-5600, JEOL, Japan) was used to observe the surface morphology of the samples.

The hydrogen generation reactions of the Al–Li alloy were carried out in a plastic reactor with a capacity of 50 ml. In each experiment, 0.2 g of Al–Li alloy powder was first placed in the reactor. Then, 20 ml of water was charged into the reactor. The generated H_2 was cooled in a water bath at room temperature and dried in a pipe filled with CaO. The volume of H_2 gas was measured by the water-displacement method, which was described in our previous study [24]. A drawing of the experimental apparatus was also presented in a previous study [25]. Under 1 atm of pressure and at 25 °C, the volume of 1 mol H_2 is 24.45 L. When 0.2 g Al–Li alloy containing a% of Al and b% of Li reacts with water to produce H_2 , the hydrogen yield is calculated as follows:

$$\text{Hydrogen yield/\%} = \frac{\text{volume of generated } \text{H}_2}{[(a\%/27) \times 1.5 + (b\%/6.9) \times 0.5] \times 24.45 \times 0.2} \quad (1)$$

In the experimental process, water with different initial temperatures and different salt solutions reacted with Al–Li alloy to produce H_2 . Additionally, the Al–Li alloy was also used to produce H_2 after being placed in the solution for different amounts of time.

3. Results and discussion

3.1. The hydrogen generation of Al–Li alloy with a low Li content

Fig. 1 presents the hydrogen-generation curves of Al–Li alloys with different Li contents, ball-milled for different times and

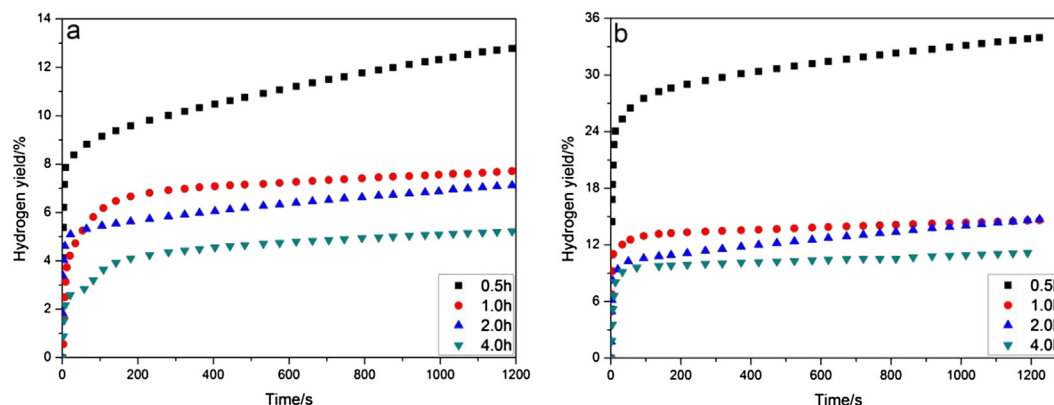


Fig. 1. Hydrogen generation of Al–Li alloys with low Li contents ball milled for different times: (a) 3%Li and (b) 5%Li.

reacted with water at 25 °C. As shown in Fig. 1(a) and (b), when the ball milling time was 0.5 h, the hydrogen-generation rate and hydrogen yield of the alloy were the highest. After reacting for 1200 s, the hydrogen yields reached 13% for Al–3%Li and 33% for Al–5%Li. However, with increasing ball-milling time, the hydrogen yields decreased gradually. As the ball-milling time reached 4.0 h, the hydrogen yields decreased to only 4% for Al–3%Li and 8% for Al–5%Li. The results show that the hydrogen-generation rate and yield of alloys with Li contents of 3 wt.% and 5 wt.% decreased with the increase in ball-milling time. Additionally, the abovementioned experimental results also demonstrate that Al–Li alloys with low Li contents demonstrate poor water splitting for the production of hydrogen.

Fig. 2(a) shows that when the ball milling time was 0.5 h, the particle size of the alloy powder was below 200 μm . However, in our previous study [21], the particle size of an Al–Li alloy with approximately 10 wt.%–20 wt.% Li was below 10 μm after ball milling for the same amount of time. As the ball-milling time was increased to 4.0 h, the particle size of Al–3%Li alloy increased significantly, reaching 400 μm . It is clear that agglomeration occurred during the ball-milling process. Additionally, as the ball-milling time was increased, the agglomeration became more distinct. From Fig. 1, it can be concluded that effect of agglomeration is adverse to the hydrogen generation of Al–Li alloys.

Fig. 3 shows an SEM image of the Al–Li alloy ball milled for 2 h. The particle size of the Al–5%Li alloy reached approximately 100 μm . As the Li content increased to 7 wt.%, the particle size was reduced to tens of micrometres. Although some small particle agglomerations remained, block-like particles could not be observed. The particle size of the Al–7%Li alloy was smaller than that of the

Al–5%Li alloy. The results indicate that increasing the Li content can reduce the size of the particles.

The Al–7%Li alloy ball milled for different times reacted with water at 25 °C to produce hydrogen; the hydrogen-generation curves of the alloy are shown in Fig. 4. According to this figure, the hydrogen yield increased with increasing ball-milling time. When the ball-milling time was 2.0 h, the hydrogen yield reached a maximum of approximately 70%. Upon further prolonging the ball-milling time, the hydrogen yield began to decrease. As the ball-milling time reached 4.0 h, the hydrogen yield decreased to approximately 45%. The effect of ball-milling time on the hydrogen yield for the Al–7%Li alloy was significantly different from that for either the Al–5%Li or –3%Li alloy. A higher hydrogen yield could be obtained due to the absence of large block-like particle agglomerations in the Al–7%Li alloy.

The abovementioned experimental results indicate that ball milling Al–Li alloys with low Li contents easily causes the agglomeration of powdered alloy particles. The lower the Li content is or the longer the ball-milling time is, the more distinct the effect of agglomeration becomes, and the hydrogen yield is accordingly reduced. Increasing the Li content can effectively eliminate the agglomeration of the alloy powder, increasing the hydrogen yield as well.

It is well known that Al exhibits good ductility and can be used as a structural material. When Al powder with a particle size of 150 μm is ball milled directly, significant agglomeration will result due to the cold welding of the Al metal. After ball milling, the particle size can increase to several centimetres. When Li is added, the metal can react with Al to form an Al–Li intermetallic compound (AlLi phase), as demonstrated in our previous research [21].

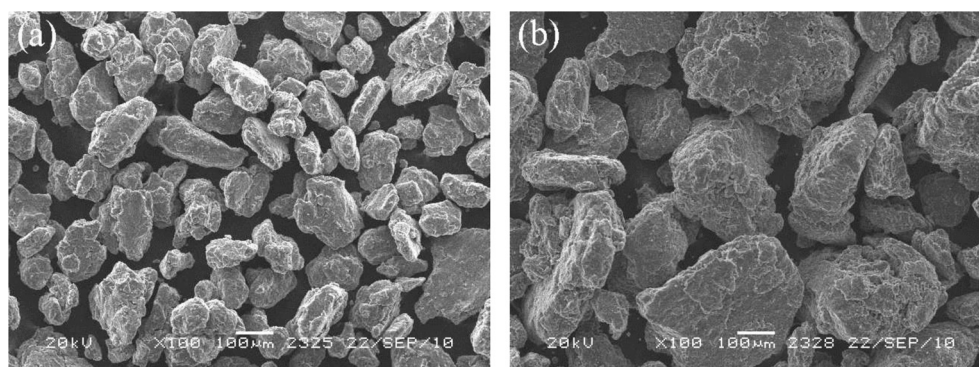


Fig. 2. SEM images of Al–3%Li alloys ball milled for (a) 0.5 h and (b) 4.0 h.

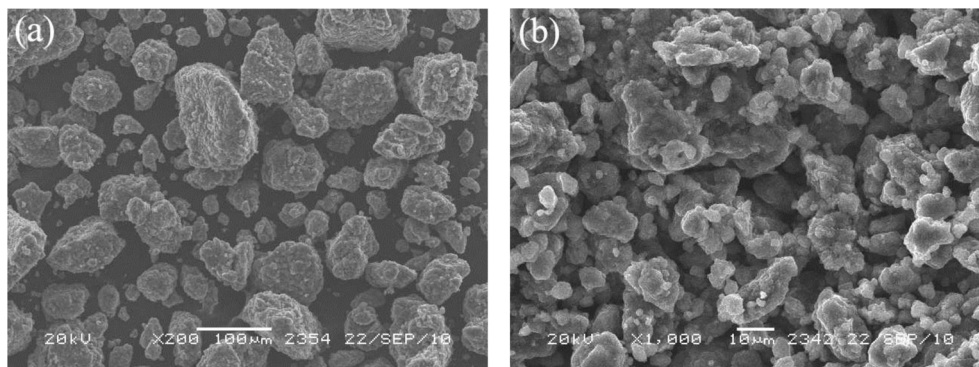


Fig. 3. SEM images of Al–Li alloys ball milled for 2 h (a) 5%Li and (b) 7%Li.

The Al–Li intermetallic compound has low mechanical strength and can be easily crushed. Therefore, the addition of Li reduces the ductility of Al, which can thus be easily crushed.

However, if the Li content is lower, the amount of Al–Li intermetallic compound formed is lower, and the resulting Al–Li alloy mainly exhibits the properties of Al. For example, when the Li content is 3 wt.% or 5 wt.%, significant agglomeration still occurs. The active intermetallic state of Al and Li will be contained within the metallic state of Al and, as a result, will be unable to react with water, which will significantly affect the generation of hydrogen. By increasing the amount of Li added, more Al–Li intermetallic compound is formed, and the Al–Li alloy gradually begins to exhibit the properties of an Al–Li intermetallic compound. The resulting Al–Li alloy will be easily crushed, which is why an Al–Li alloy with approximately 10 wt.%–20 wt.% Li can be crushed into particles measuring several micrometres and a 100% hydrogen yield can be obtained.

Based on the foregoing analysis, the agglomeration of Al–Li alloys with low Li contents significantly reduces the hydrogen yield thereof. Only by eliminating the agglomeration of Al–Li alloy that results from the use of low Li contents can a high hydrogen yield be obtained, resulting in the rapid generation of hydrogen.

3.2. Modification of Al–Li alloy with a low Li content

When preparing materials by the ball-milling method, small amounts of process-control agents are added to eliminate

agglomeration by inhibiting the cold welding of the working powder. In our previous studies [24,25], NaCl was used as an effective process-control agent to improve the hydrogen generation of Al–Ca alloy and Al–CaO materials. In this study, NaCl was introduced into Al–Li alloys with low Li contents during ball milling to eliminate agglomeration and improve the reactivity of the resulting Al–Li alloys.

3.2.1. Effect of the NaCl addition

Fig. 5 shows an SEM image of an Al–5%Li alloy with different amounts of added NaCl, ball milled for 2.0 h. When NaCl was not added, the particle size of the alloy powder nearly exceeded 50 µm (Fig. 5a). After 1 wt.% NaCl was added, the particle size was significantly reduced to approximately 10–20 µm, and only a few larger particles could be identified. By increasing the amount of NaCl added, the particle size could be further reduced. As the amount of NaCl added was increased to 5 wt.%, the alloy particle size was reduced to below 10 µm. The results indicate that NaCl can prevent particle agglomeration and reduce the particle size of alloys during the process of ball milling. As the amount of NaCl added was increased, the particle size became. NaCl crystals are brittle and easily crushed under the mechanical forces experienced during ball milling. Thus, crushed NaCl powder will disperse on the surfaces or in the cracks of alloy particles, which effectively inhibits the cold welding of metal and prevents the agglomeration of alloy particles during the process of ball milling.

After ball milling for 2.0 h with NaCl, the Al–Li alloys were reacted with water to produce hydrogen at 25 °C. The effects of NaCl addition on the hydrogen generation of Al–Li alloys are shown in Fig. 6. According to the figure, the hydrogen-generation rate and hydrogen yield increased with the increasing addition of NaCl. For the Al–3%Li alloy (Fig. 6a), the hydrogen yield increased to approximately 70% after the addition of 3 wt.% NaCl. Compared with that obtained with no NaCl addition, the hydrogen yield was significantly improved. As the NaCl addition reached 7 wt.%, the hydrogen yield was improved to 95.8%. Due to the effect of NaCl addition, the hydrogen yield of the Al–3%Li alloy could be increased to 100% as long as the amount of NaCl added as suitable. Additionally, for the Al–5%Li alloy (Fig. 6b), when 1 wt.% NaCl was added, the hydrogen yield increased from 15% to 45% upon reaction with water for 2000 s. Furthermore, 100% hydrogen yield could be obtained after adding 3 wt.% and 5 wt.% NaCl. However, the hydrogen-generation rate of Al–5%Li–5%NaCl was higher. The results indicate that NaCl addition can improve the hydrogen generation of Al–Li alloys with low Li contents. NaCl cannot only raise the hydrogen yield of alloys but also enhance the hydrogen-generation rate thereof.

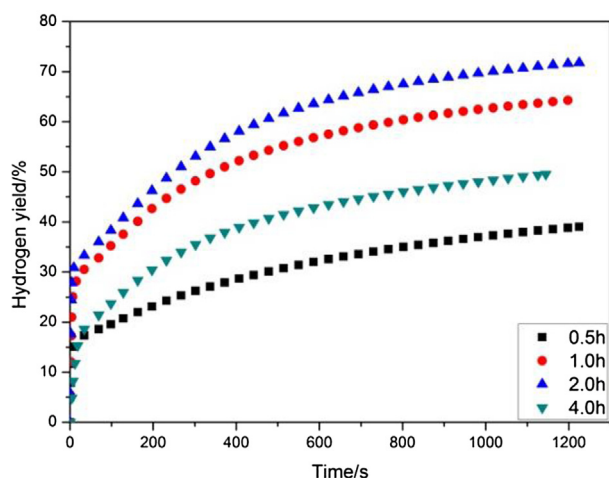


Fig. 4. Hydrogen generation of Al–7%Li alloys ball milled for different times.

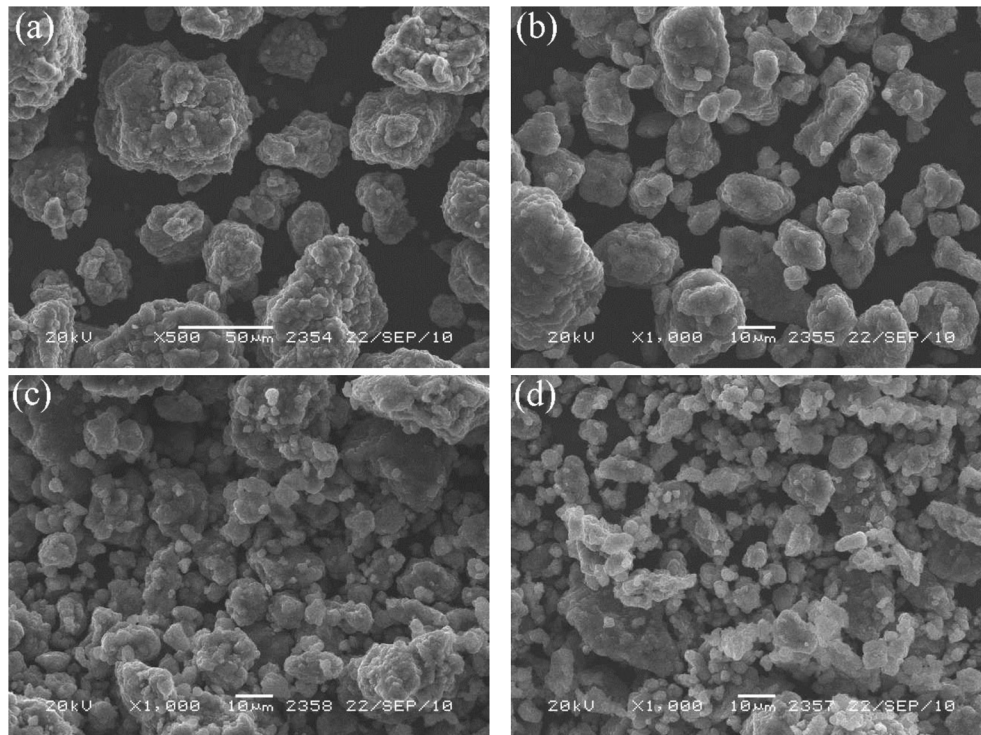


Fig. 5. SEM images of Al–5%Li alloys with different amounts of added NaCl: (a) 0%NaCl, (b) 1%NaCl, (c) 3%NaCl and (d) 5%NaCl.

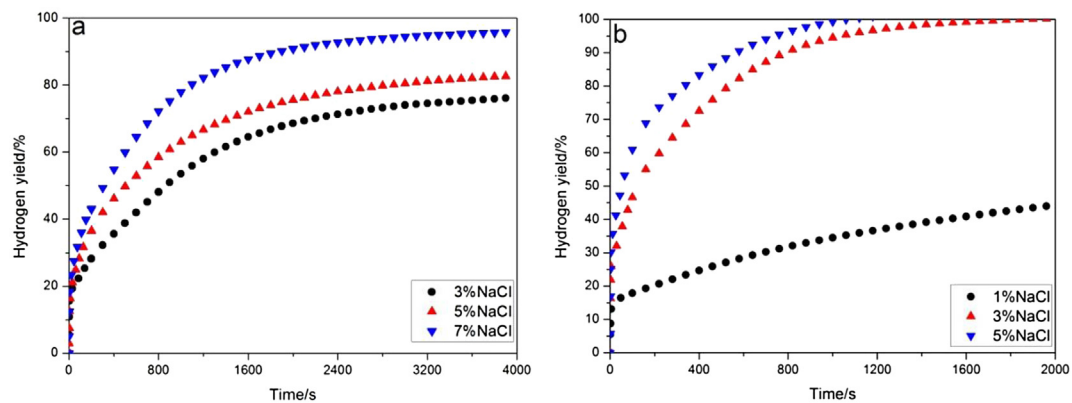


Fig. 6. Effect of NaCl addition on hydrogen generation of Al–Li alloys activated by adding NaCl: (a) 3%Li and (b) 5%Li.

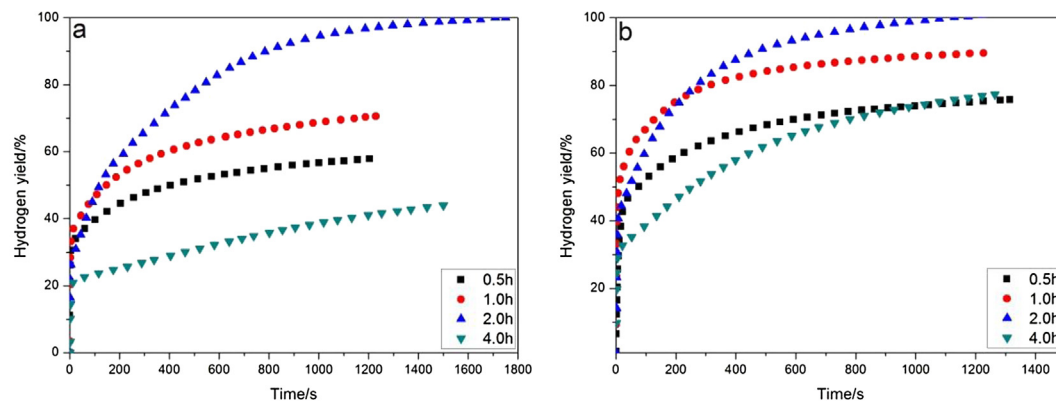


Fig. 7. Effect of ball-milling time on hydrogen generation of Al–Li–NaCl alloys: (a) Al–5%Li–3%NaCl and (b) Al–7%Li–3%NaCl.

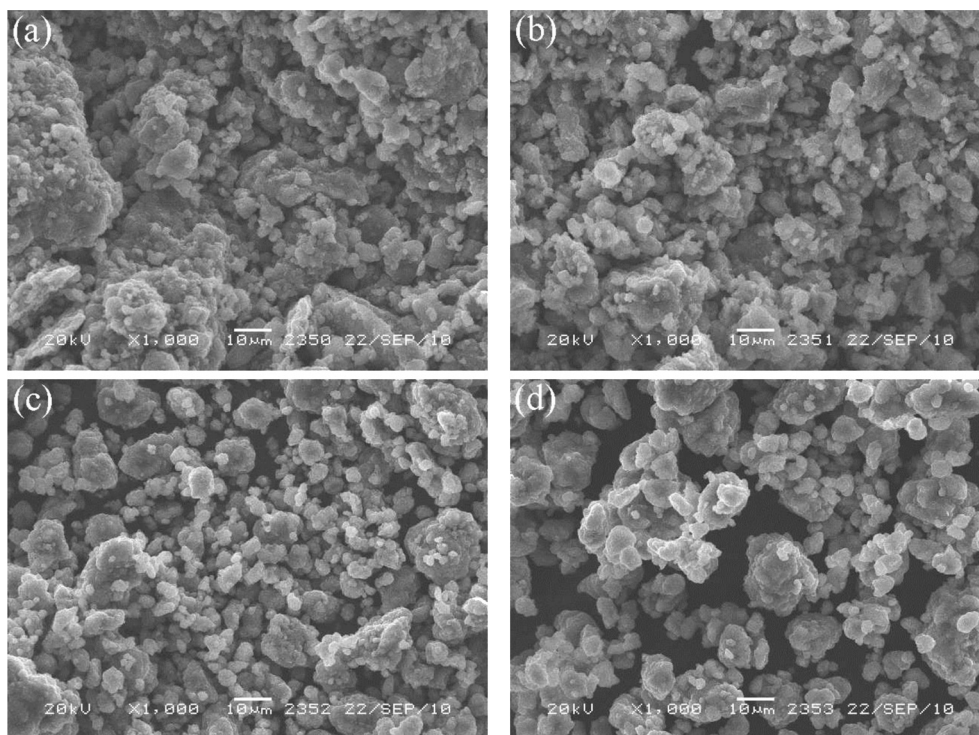


Fig. 8. SEM images of Al–7%Li–3%NaCl ball milled for (a) 0.5 h, (b) 1.0 h, (c) 2.0 h and (d) 4.0 h.

3.2.2. Effect of the ball-milling time

After ball milling for different times, the Al–Li–NaCl alloys were reacted with water to produce hydrogen at 25 °C. Fig. 7 presents the hydrogen-generation curves of Al–5%Li–3%NaCl and Al–7%Li–3%NaCl reacting with water. As shown in the figure, the hydrogen yield first increased with increasing ball-milling time. For the Al–5%Li–NaCl alloy (Fig. 7a), the effect of ball-milling time on hydrogen generation was significantly different from that observed for Al–5%Li (Fig. 1(a)). This result again demonstrates that NaCl plays an important role in hydrogen generation. As the ball-milling time was increased to 2.0 h, the hydrogen yield reached a maximum of 100%. By contrast, the hydrogen-generation rate of Al–7%Li–3%NaCl was higher. A hydrogen yield of 100% could be obtained by reacting with water for approximately 1200 s.

However, by further prolonging the ball-milling time, the hydrogen yield began to decrease. As the ball-milling time reached 4.0 h, the hydrogen yield decreased to approximately 42% for Al–5%Li–3%NaCl over 1500 s and 80% for Al–7%Li–3%NaCl over 1300 s.

Fig. 8 presents an SEM image of Al–7%Li–3%NaCl ball milled for different times. When the ball-milling time was 0.5 h, although some larger particles were still present, particles below 10 µm in size could be observed. With increasing ball-milling time, the particle size of the alloy powders gradually decreased. As the ball-milling time reached 2.0 h (Fig. 8c), a significant amount of the particles measured less than 10 µm. Compared with that of the alloy to which no NaCl was added (Fig. 3b), the particle size was significantly reduced, allowing the hydrogen yield to reach 100% quickly. However, as the ball-milling time was prolonged to 4.0 h, the alloy powder aggregated into larger particles, reducing the hydrogen yield. From the hydrogen-generation curves of Al–5%Li–3%NaCl (Fig. 7a), it can be deduced that the effects of the ball-milling time on the morphology of the alloy with a low Li content are similar to those observed for Al–5%Li–3%NaCl. The experimental results show that the size of the particles first decreased and then increased with ball-milling time.

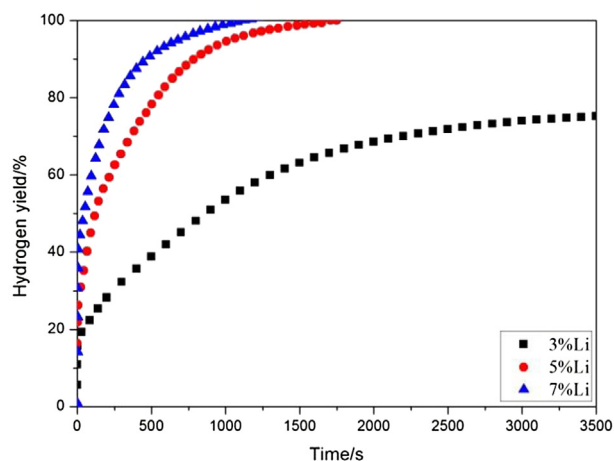


Fig. 9. Effect of Li content on hydrogen generation of Al–Li–3%NaCl ball milled for 2.0 h.

Table 1

Ultimate hydrogen yield of Al–Li alloys prepared under different conditions.

Sample		Hydrogen yield/%			
Li content/wt.%	NaCl addition/wt.%	0.5 h	1.0 h	2.0 h	4.0 h
3	3	37.26	43.23	70.25	12.88
3	5	45.75	—	82.82	—
3	7	58.49	—	95.81	—
5	3	57.85	70.60	100	47.68
5	5	67.60	—	100	—
5	7	71.20	—	—	—
7	3	75.77	89.61	100	77.34
7	5	74.82	—	100	—
7	7	82.83	—	—	—

The abovementioned results indicate that the ball-milling time significantly affected the hydrogen generation of Al–Li–NaCl alloys. Indeed, a ball-milling time that is too long will not be favourable to the hydrogen generation of Al–Li alloys.

3.2.3. Effect of the Li content

Fig. 9 depicts the hydrogen-generation curves of Al–Li–3%NaCl with different Li contents, ball milled for 2.0 h and reacted with water at 25 °C. When the Li content was 3%, the hydrogen yield could reach 60% upon reacting for 1200 s. The hydrogen-generation reaction reached equilibrium within 3500 s, and the ultimate hydrogen yield was 76.08%. As the Li content was increased to 5%, the reaction rate improved significantly. A hydrogen yield of 100% could be achieved after reacting for only 1700 s. After the Li content was increased further to 7%, the reaction time necessary to obtain a hydrogen yield of 100% was shortened to 1200 s. The experimental results indicate that the hydrogen yield and reaction rate of Al–Li alloys can be improved with increasing Li content because Li itself is an active metal and can activate Al.

To comprehensively understand the effects of Li content, NaCl addition and ball-milling time on hydrogen generation, the Al–Li alloys prepared under different conditions were reacted with water to produce hydrogen at 25 °C. Table 1 presents the ultimate hydrogen yield of the Al–Li alloys. It can be concluded that as the Li content is reduced, more NaCl must be added to obtain a high hydrogen yield. Similarly, as the Li content is increased, only a small amount of NaCl must be added to reach a high hydrogen yield. The results indicate that the Li content, NaCl addition and ball-milling time have significant effects on the hydrogen generation of Al–Li alloys.

Based on the abovementioned experimental results, it can be concluded that Al–Li alloys with low Li contents were successfully activated by adding NaCl. The hydrogen-generation rate and hydrogen yield were significantly improved, and the ultimate hydrogen yields could reach 100% as long as the appropriate amount of NaCl was added.

3.3. Effect of the initial water temperature

Mobile hydrogen production must be able to operate during different seasons. Therefore, the technology demands that hydrogen-generating materials be able to react with water to produce hydrogen quickly at different initial temperatures. Fig. 10

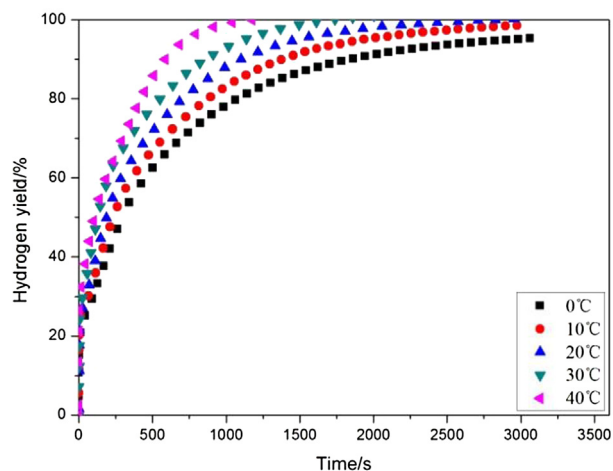


Fig. 10. Effect of initial water temperature on hydrogen generation of Al–5%Li–3%NaCl ball milled for 2.0 h.

presents the hydrogen-generation curves of Al–5%Li–3%NaCl reacted with water at different initial temperatures. The figure indicates that after reacting for 3000 s at 0 °C, the hydrogen yield of the alloy decreased slightly relative to that at 25 °C, but the yield was still capable of reaching 95%. As the initial water temperature was increased to 10 °C, the hydrogen yield reached 100% within the same amount of time. By increasing the initial water temperature further, the hydrogen-generation rates were gradually enhanced. As the water temperature reached 40 °C, a hydrogen yield of 100% could be obtained after reacting for 1000 s. The results show that higher water temperatures are beneficial for increasing the hydrogen-generation rate. The process of hydrogen generation achieved by reacting Al–Li alloys with water belongs to the class of exothermic reactions. A significant amount of heat is released during the process of hydrogen generation, thus heating the surrounding water. Even when the temperature of the water is initially 0 °C, as long as the reaction can be initiated, the water temperature will rise. Therefore, the initial water temperature does not affect the hydrogen generation of Al–Li alloys, which indicates that Al–Li alloys exhibit stronger adaptability to different water temperatures.

3.4. Effect of different water solutions

After activation with NaCl, Al–Li alloys with low Li contents could react with pure water to produce hydrogen quickly. However, in some special situations, pure water could not be obtained, and Al–Li alloys could only react with water solutions containing impurities to produce hydrogen. Therefore, it was necessary to investigate the effects of solution composition on the hydrogen generation of the alloys. Water solutions with different compositions were prepared by adding 1.0, 0.5, 1.0, 0.5, and 1.0 mol L^{−1} of NaCl, CaCl₂, Na₂SO₄, MgCl₂ and NaNO₃, respectively. The hydrogen-generation curves for Al–7%Li–3%NaCl alloy reacted with different salt solutions at 25 °C are shown in Fig. 11. As shown in the figure, when the alloy was reacted in the NaCl and Na₂SO₄ solutions, the hydrogen generation was minimally affected. A hydrogen yield of 100% could be achieved by reacting for 1600 s and 2200 s. However, as the Al–Li alloy reacted with water solutions containing CaCl₂, MgCl₂ and NaNO₃, the hydrogen yield was significantly reduced to 61.8%, 44% and 58.2%, respectively. During hydrogen generation, Al–Li alloys reacted with water can produce OH[−] on the surfaces of the alloy particles. Ca²⁺ and Mg²⁺ can combine with OH[−] to form Ca(OH)₂ and Mg(OH)₂. The insoluble compound will coat the

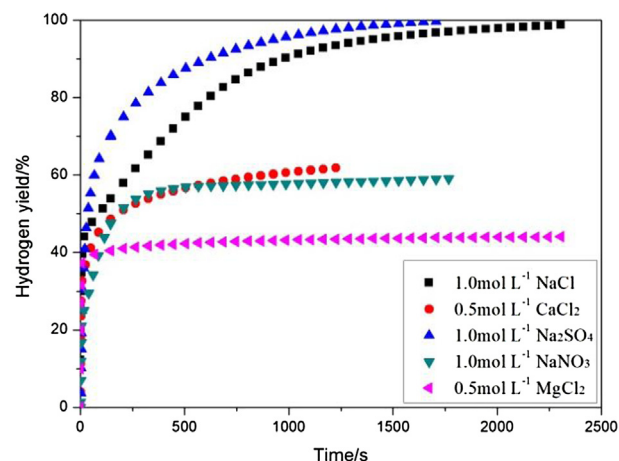


Fig. 11. Effect of different salt solutions on hydrogen generation of Al–7%Li–3%NaCl alloy ball milled for 2.0 h.

surfaces of the alloy particles, preventing hydrogen generation. Additionally, NO_3^- can react with Al to form ammonia [26]. A portion of the Al is consumed and cannot produce hydrogen. Therefore, to achieve a high hydrogen yield, Al–Li alloys should not react with water solutions containing Ca^{2+} , Mg^{2+} and NO_3^- .

3.5. Effect of air exposure

The abovementioned experimental results demonstrate that the reactivity of Al–Li alloys with low Li contents is significantly improved by adding NaCl during the ball-milling process. Although the improvement in reactivity aids hydrogen generation, the Al–Li alloys are also likely to oxidise easily. It is well known that air contains moisture and O_2 , which can react with Al–Li alloys, making air adverse for the safe storage of alloys. Therefore, it was necessary to investigate the effect of air exposure on the hydrogen generation of Al–Li alloys. Al–3%Li–7%NaCl alloy ball milled for 2.0 h was exposed to air with a moisture content of 50 RH% at 30 °C for different times and then reacted with water to generate hydrogen. Fig. 12 exhibits the hydrogen-generation curves of alloys exposed to air for different times. The figure shows that as long as the air exposure time did not exceed 4.0 h, the hydrogen generation rate was not significantly altered, and the ultimate hydrogen yield could still exceed 90%. When the air exposure time reached 8.0 h, the hydrogen-generation rate was significantly reduced, and the hydrogen yield was decreased to approximately 85%. By further prolonging the air-exposure time, the hydrogen-generation rate and hydrogen yield were also reduced further. When the alloy was placed in air for 24 h, the ultimate hydrogen yield was only approximately 67%. The results indicate that Al–3%Li–7%NaCl alloys can be oxidised by air over longer air exposure times, reducing the ultimate hydrogen yield accordingly. Therefore, Al–Li alloys with low Li contents should be stored in isolation from air to maintain good hydrogen-generation performances.

4. Conclusions

In this study, Al–Li alloys with low Li contents were successfully prepared by the ball-milling method and could quickly react with water to produce hydrogen. The results of the study demonstrate that the addition of NaCl can effectively enhance the reactivity of Al–Li alloys with low Li contents and can

improve the hydrogen generation thereof. By increasing the amount of NaCl added, the hydrogen-generation rate and hydrogen yield can be increased. Prolonging the ball-milling time is beneficial for decreasing the particle size of the alloys and increasing their activity. However, excessively long ball-milling times can easily cause alloy particle agglomeration and consequently affect the hydrogen yield. The optimal ball-milling time was determined to be 2.0 h. It was also observed that the hydrogen-generation rate increases with the increase in Li content. Under the optimal preparation conditions, the ultimate hydrogen yield could reach 100% for Al–Li alloys with low Li contents. Al–Li alloys with low Li contents could quickly react with water at different initial temperatures to produce hydrogen, even at 0 °C. Moreover, different water solutions affect the hydrogen generation of Al–Li alloys. Ca^{2+} and Mg^{2+} can combine with OH^- to form the insoluble compounds $\text{Ca}(\text{OH})_2$ and $\text{Mg}(\text{OH})_2$, which then cover the surfaces of the alloy particles, preventing hydrogen generation. NO_3^- reacts with Al to form ammonia, thus reducing the hydrogen yield. Therefore, Al–Li alloys should be prevented from reacting with water containing Ca^{2+} , Mg^{2+} and NO_3^- . Al–Li alloys with low Li contents are highly reactive and must be stored in isolation from air to maintain good hydrogen-generation performances.

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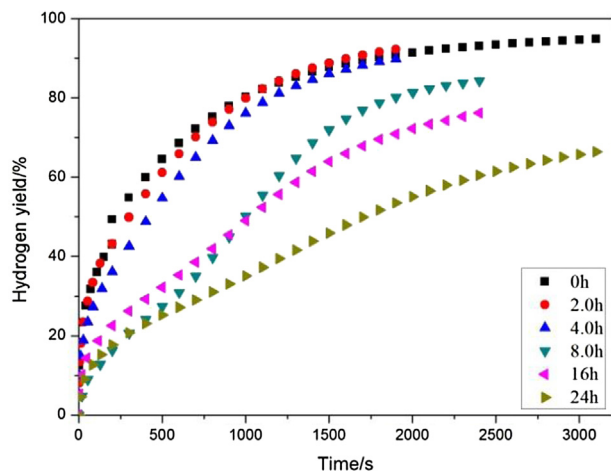


Fig. 12. Hydrogen generation of Al–3%Li–7%NaCl alloy (ball milled for 2 h) placed in air for different times.